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(54) Title: SPECTROMETER

(57) Abstract

The spectrometer comprises a radiation source (1) whose radiation is focused on an entrance slit (5) of an echelle monochromator (6, 7, 8, 9, 10). A fibre optic bundle (52) has one end (51) located above a slot on the output plate (10) of the echelle monochromator and its other end (53) located adjacent an array detector (54). The fibre optic bundle (52) has a card (59) attached to it which specifies the respective positions of the ends of each fibre within the bundle. A card reader (58) reads this information and passes it to a memory (61). A microprocessor (57) is used to relate the outputs of a given detector element to a given wavelength of radiation using the information read from the card (59).

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SPECTROMETER

BACKGROUND OF THE INVENTION

The invention relates to a spectrometer comprising means for gathering radiation emanating from or passing through a sample, means for selecting radiation of a given band of wavelengths, and means for directing the selected radiation onto a detector.

The invention is of particular though not exclusive use in an atomic emission spectrometer. In such instruments the wavelengths to be detected are commonly separated by means of an echelle monochromator. This will include an echelle grating and an order sorting prism so that the different orders of diffraction coming from the echelle grating are dispersed at right angles by the order sorting prism. The spectra produced by the various orders of diffraction are then spaced across an output aperture plate.

DESCRIPTION OF PRIOR ART

In a known spectrometer of this type, an example of which is the Unicam PU 7000 ICP atomic emission spectrometer, the detector of radiation is a photomultiplier tube which is mounted on a carriage which can be moved to any point on the aperture plate so that a selected aperture allows radiation of a given wavelength through to the photomultiplier tube. With this arrangement it is only possible to detect a single wavelength or narrow band of wavelengths at one time. In principle it would be possible to provide a plurality of photomultiplier tubes each with their own separate carriage so that more than one wavelength could be detected simultaneously. However in practice such an arrangement would be too expensive and bulky.

Another construction for an atomic emission spectrometer which has been proposed is to focus the echelle output spectrum onto a two dimensional array of charge coupled devices (CCDs). Such arrays are readily available since they are commonly used as sensors for video

cameras. However this requires accurate focusing of the echelle output image onto the CCD array and places certain restraints on the physical layout of the instrument.

SUMMARY OF THE INVENTION

According to this invention a spectrometer comprising means for gathering radiation emanating from or passing through a sample, means for selecting radiation of a given band of wavelengths, and means for directing the selected radiation onto a detector, is characterised in that the detector comprises an array of solid state detector elements and in that the means for directing the radiation onto the detector comprises a plurality of optical waveguides, each element of the array receiving radiation from one or more optical waveguides.

An advantage of this invention is that it enables a dispersed spectrum of radiation to be detected by an array detector while allowing greater flexibility of instrument layout.

The plurality of optical waveguides preferably comprise an optical fibre bundle.

By using optical fibres to carry the radiation from the output of the radiation selecting means it is possible to locate the detectors more flexibly. Thus it is not necessary to be able to focus the radiation from the output of the monochromator onto the detector and there does not need to be a clear path to the detector. By providing a bundle of optical fibres coupled to an array detector it is possible to detect simultaneously a band of wavelengths and consequently in an atomic emission, absorption, or fluorescence spectrometer simultaneous measurements for a number of elements may be made. As the fibre optic bundles are compact and flexible it is possible to provide a plurality of bundles, on for example an echelle output plate, and if a corresponding plurality of detector arrays is provided then even greater flexibility in simultaneous measurement of a plurality of sample elements can be made.

The optical fibres may be clamped in a fixed orientation and position at each end, the position of individual fibres being the same at both ends. Thus the spectrum at the output slit is transferred to the detector array coherently, that is as though the exit slit was focused on the array. In this case it is not necessary for there to be a single optical fibre corresponding to a single detector element and in particular, a plurality of fibres could be coupled to each detector element. This eases alignment problems between the end of the optical fibre bundle and the detector.

The optical fibres of the bundle may be held in a fixed orientation and position at each end, the position of individual fibres at one end being randomly related to that of the corresponding fibre at the other end, the spectrometer further comprising means for determining which fibres correspond to a given wavelength of received radiation.

Constructing bundles of fibre optic cables which are coherent, that is where the fibre position at one end corresponds to that at the other end is relatively expensive whereas if the fibres are allowed to arrange themselves randomly a much less expensive manufacturing method can be used to construct the fibre bundle. By determining the relative alignments of the fibres at each end and providing in the spectrometer means for correcting the input signal from the detector in accordance with the position of the fibres, it is possible to use relatively inexpensive fibre optic bundles.

The determining means may comprise a microprocessor and memory means, the memory means containing data defining the positions of each individual fibre in the bundle at both ends. The fibre bundle may have associates with it coding means which enables the data to be read into the memory means.

The data may be coded in machine readable form for example on a magnetic card, or may be in written form

whereby the operator enters the information into the spectrometer via a keyboard.

BRIEF DESCRIPTION OF DRAWINGS

The above and other features of the invention will become more apparent from the following detailed description of embodiments of the invention, which is given by way of example, with reference to the accompanying drawings, in which:-

Figure 1 shows in block schematic form a known atomic emission spectrometer;

Figure 2 shows schematically a modification of the spectrometer of Figure 1 to produce a spectrometer in accordance with the invention;

Figures 3 and 4 show first and second arrangements for determining the relative positions of individual fibres at each end of a fibre optic bundle; and,

Figure 5 shows in block schematic form a spectrometer according to the invention.

DESCRIPTION OF PREFERRED EMBODIMENT

Figure 1 shows in block schematic form an atomic emission spectrometer which comprises a source unit 1 and a detector unit 2. The source unit 1 includes an inductively coupled plasma torch 3 in which the sample is atomised. Radiation emitted by the sample is passed to a focusing mirror 4 which focuses the radiation on the entrance slit 5 of an echelle monochromator. Radiation passes through the entrance slit 5 onto a collimating mirror 6 which directs the radiation to an echelle grating 7. Dispersed radiation from the echelle grating 7 passes through an order sorting prism and focusing lens 8 onto a plane mirror 9. The plane mirror 9 reflects the dispersed radiation onto an aperture 10 which forms a plurality of exit slits from the monochromator. A detector 11 in the form of a photomultiplier tube is arranged over a selected slit in the aperture plate 10 to detect radiation of a given wavelength. The detector 11 is mounted on a carriage which is controlled so that it can place the detector over

a selected slit on the plate. A spectrometer as described with reference to Figure 1 has been manufactured and sold by Unicam Limited under the type number PU 7000.

Figure 2 shows how this spectrometer may be modified according to the invention. The aperture plate 10 instead of having a large number of small apertures, each of which lets through a single wavelength, or narrow band of wavelengths, is provided with a plurality of slots 20, 21,22,23 each of which is dimensioned so that a full spectrum of a given order is let through. An optical fibre bundle 24 is clamped at one end 25 and located over the slot 23. A similar clamping arrangement 26 at the other end is located over a diode array detector 27. Thus each individual fibre and its associated element of the diode array detector 27 corresponds to the slit and photomultiplier tube of the arrangement of Figure 1. If the bundle is coherent, that is, the positions of the ends of individual fibres correspond at both ends of the bundle, then a plurality of fibres may be coupled to each element of the diode array 27. This eases alignment problems as it is not essential that a given fibre completely aligns itself with a single element of the array. However, if the optical fibre bundle 24 is not coherent, that is the positions of the ends of a single fibre do not correspond at both ends of the bundle, it is then necessary that only a single fibre is coupled to a given detector element.

If a coherent fibre optic bundle is provided the spectrometer becomes equivalent to one where the diode array is either mounted on the output slit or has an image of the output slit focused on it and standard diode array detection electronics can be used. However such a bundle is expensive to produce and it would be advantageous if a non-coherent bundle could be manufactured and used. To enable such a bundle to be used it is proposed to determined the position, at each end of the bundle, of the end of each fibre and to use this information to modify the processing of the signal produced by the detector.

Figures 3 and 4 illustrate two methods of determining the relative positions of the fibre ends. As shown in Figure 3 a stationary light source 30 provides radiation which is directed onto one end 31 of a fibre optic bundle 32. Between the radiation source 30 and the end 31 of the fibre optic bundle 32 is a shutter 33. The shutter is moved to expose in turn the ends of each of the optical fibres in the bundle 32. A detector 35 is positioned at the other end 34 of the fibre optic bundle. This may be a standard diode array detector of the form which will be used in the spectrometer. By moving the shutter 33 and monitoring at the detector 35 which elements are illuminated as the shutter is moved, the corresponding positions of the ends of the fibres at each end of the bundle can be determined. This information can then be stored and used to calibrate the spectrometer.

Figure 4 shows an alternative way of calibrating the fibre optic bundle. This uses a moveable radiation source 40 and a coherent bundle 41 of optical fibres. The bundle has one end 42 splayed out so that individual fibres are relatively widely separated and another end 43 which is clamped so that the ends of the fibres align with the ends 44 of a non-coherent optical fibre bundle 42. The other end 45 of the non-coherent bundle 42 is coupled to a diode array detector 46. By aligning the radiation source 40 with each individual fibre at the end 42 in turn and detecting which element of the diode array 46 received radiation, positions of the ends of each optical fibre in the bundle 42 can be determined. This information can then be stored and used to calibrate the spectrometer.

When the fibre optic bundle has been calibrated, it is possible to attach to it a label which contains the calibration information. This may be, for example, in the form of a magnetically encoded card or may have the information printed so that an operator can key appropriate instructions into the spectrometer manually. If a magnetically or optically encoded card is used this can

then be inserted into a card reader on the spectrometer and the information automatically read by the reader and entered into the spectrometer without requiring the intervention of an operator other than to insert the card in a reader.

Figure 5 shows in block schematic form an embodiment of a spectrometer according to the invention. It comprises a source unit 1 and detector unit 2 which are as described with reference to Figure 1 except that the aperture plate 10 is of the form shown in Figure 2. One end 51 of an optical fibre bundle 52 is aligned over one of the slots in the aperture plate 10 and its other end 53 is aligned with a diode array detector 54. The diode array detector is connected to a control and read out circuit 55 which contains the electronics for scanning the diode array and converting the signals read out from the diode array into digital form so that it can then be passed via a bus 56 to a microprocessor 57. A card reader 58 is arranged to read information from a card 59 which is attached to the bundle 52. This information is stored in a memory 61, which is also attached to the bus 56, under the control of the microprocessor 56. Also attached to the bus 56 is a keyboard 62 and display unit 63. The microprocessor memory and keyboard are also used to control other functions of the spectrometer in a known manner and to analyse the results for display on the display unit 63 or to send the results to a printer (not shown) which provides a hard copy version of the results.

It would be possible to modify the arrangement shown in Figure 5 by providing a plurality of bundles of optical fibres with a corresponding plurality of detector arrays. Alternatively if a single two dimensional detector array was used the fibre optic bundles could be aligned with different parts of the array. Either a plurality of card readers could be employed or a single card reader could be used to read the cards attached to each of the optical fibre bundles in turn during the initial setting setting up

procedures of the instrument. Clearly the detector array 54 need not be a photodiode array but could be a charge coupled device array or any other convenient array of detector elements.

The invention is not limited to use in atomic emission spectrometers but could be used in any spectrometer which used an array of detector elements.

As an alternative to the methods of determining the position of the individual fibres of the bundle described with reference to Figures 3 and 4 it would be possible to calibrate the spectrometer directly. For example one end of the bundle could be traversed across a narrow output slit of the monochromator in the spectrometer and the order of illumination of detector elements read directly into the memory 61. This would eliminate the need for a card reader or for manual entry of the information. An interlock could be built in to ensure that when a fibre optic bundle was changed the calibration operation has to be repeated.

CLAIMS

1. A spectrometer comprising means (4,5) for gathering radiation emanating from or passing through a sample, means (6,7,8,9,10) for selecting radiation of a given band of wavelengths and means for directing the selected radiation onto a detector (27,54); characterised in that the means for directing the radiation onto the detector (27,54) comprises a plurality of optical waveguides (24,52), each element of the array receiving radiation from one or more optical waveguides (24,52).

2. A spectrometer as claimed in claim 1, wherein the plurality of optical waveguides comprises a fibre optic bundle (24,52).

3. A spectrometer as claimed in claim 2, wherein at each end of the bundle (24,52) the optical fibres are clamped in a fixed orientation and position, the relative position of each individual fibre being the same at both ends.

4. A spectrometer as claimed in claim 2, wherein at each end of the bundle (24,52) the optical fibres are held in a fixed orientation and position, the relative position of individual fibres at one end being randomly related to that at the other end, the spectrometer further comprising means (56,58,59,61) for determining which fibre corresponds to a given wavelength of received radiation.

5. A spectrometer as claimed in claim 4, wherein the determining means comprises a microprocessor (56) and memory means (61), the memory means (61) containing data defining the positions of the individual fibres in the bundle (24,52).

6. A spectrometer as claim in claim 5, in which the optical fibre bundle (24,52) has associated with it coding means (59) which enables the data to be read into the memory means (61).

7. A spectrometer as claimed in claim 6, in which the coding means comprises a magnetic card (59) and the spectrometer further comprises a magnetic card reader (58).

Fig.1.

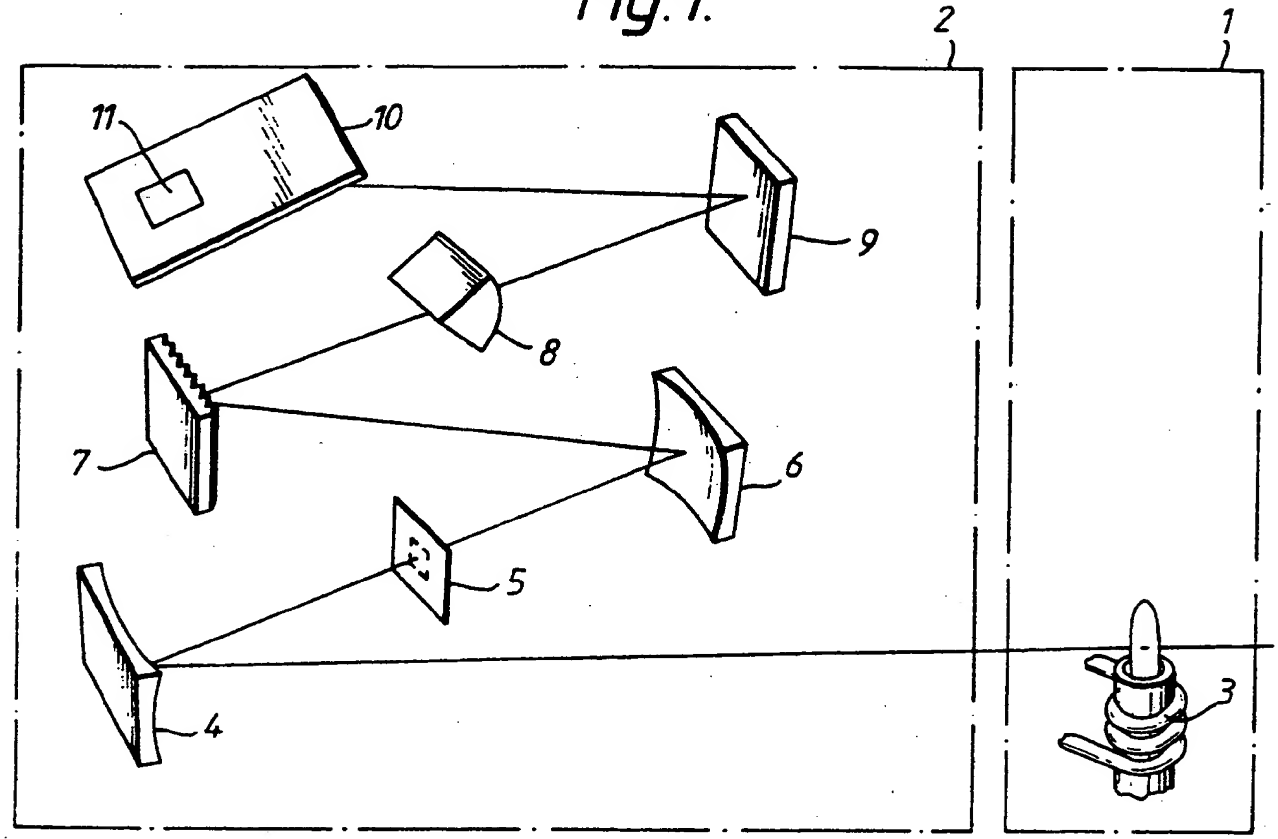


Fig.2.

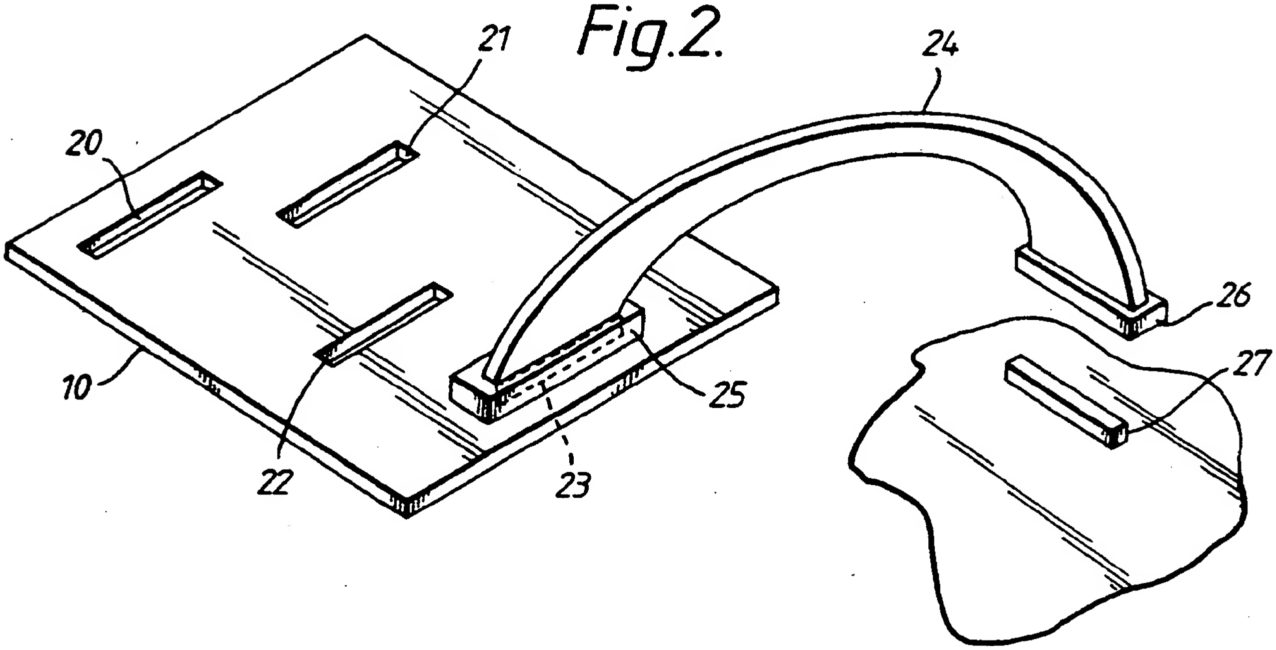


Fig.3.

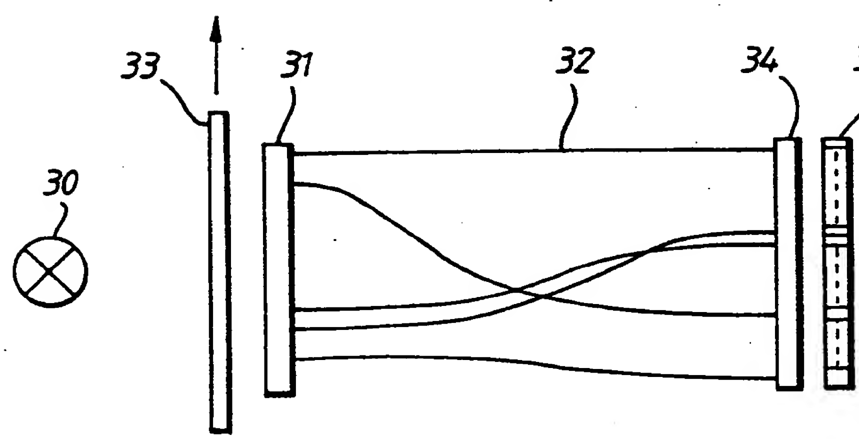


Fig.4.

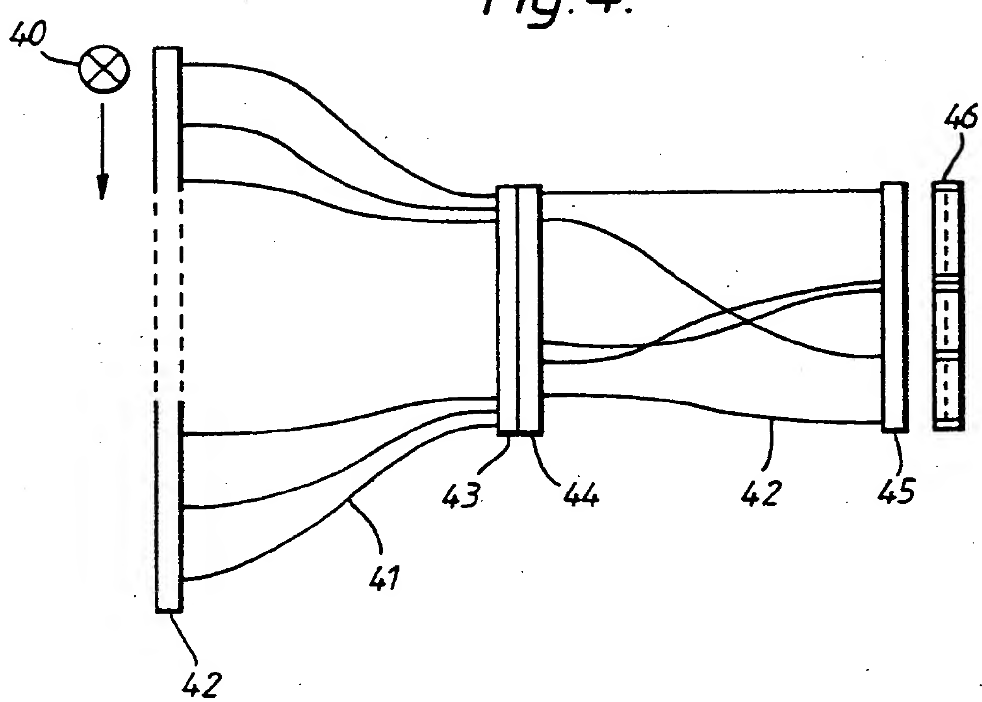
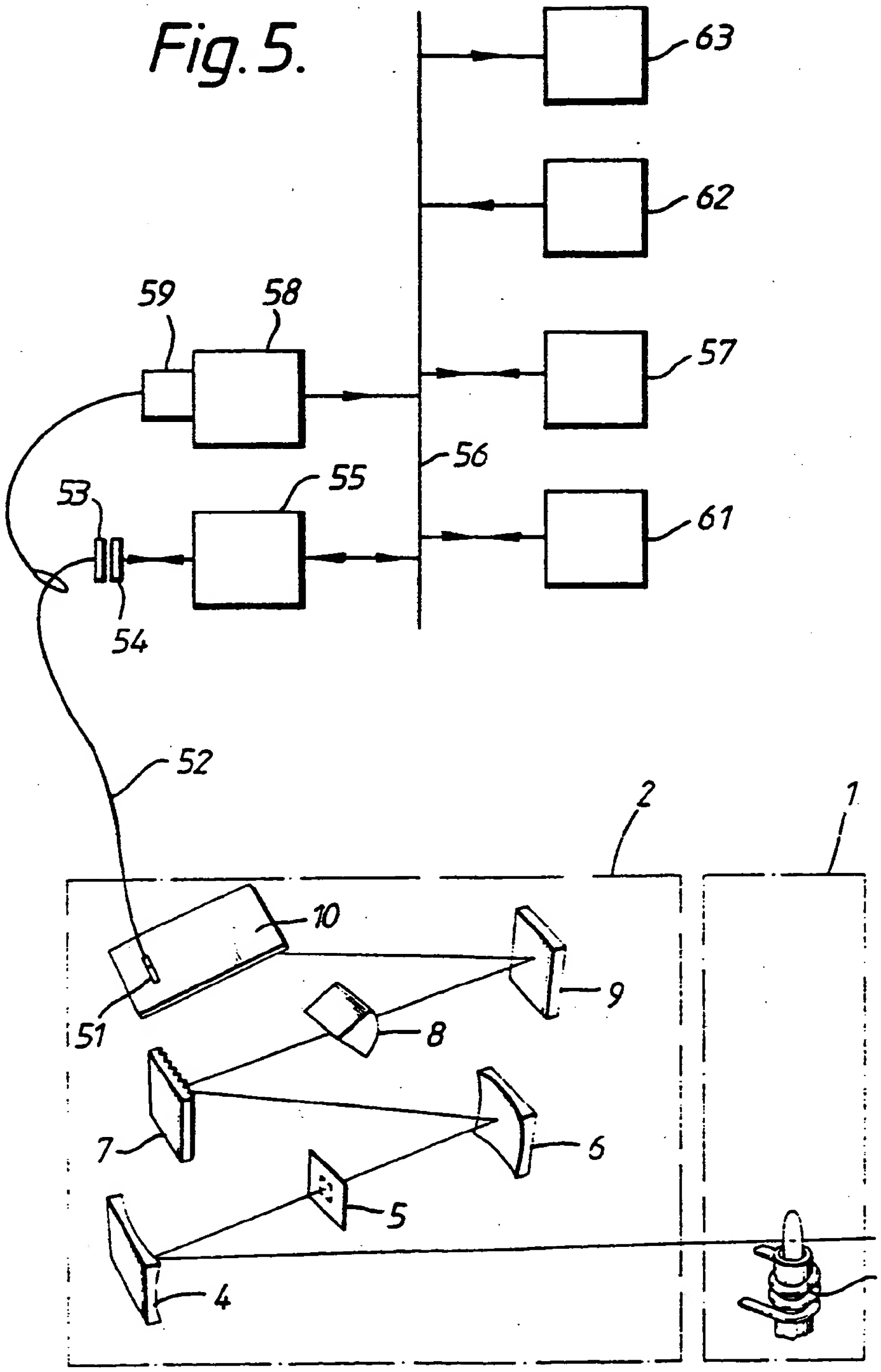


Fig. 5.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 91/02260

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 G01J3/28

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	G01J ; G02B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	EP,A,0 362 562 (F.KRUPP GMBH) 11 April 1990 see column 1 - column 3 ---	1-3
X	REVIEW OF SCIENTIFIC INSTRUMENTS vol. 57, no. 8, 1 August 1986, pages 2035 - 2037; N.HAWKES ET AL.: 'MULTICHANNEL DETECTOR FOR UV' see page 2035 - page 2036 ---	1-3
X	REVIEW OF SCIENTIFIC INSTRUMENTS vol. 57, no. 8, 1 August 1986, pages 1816 - 1818; R.KINDSFATHER ET AL.: 'TWO DIMENSIONAL THOMSON SCATTERING SYSTEM' see page 1816, paragraph III - page 1817 ---	1
X	FR,A,2 097 106 (COATS LTD) 3 March 1972 see page 6 - page 9; figures 2-4 --- -/--	1-3

° Special categories of cited documents : [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
24 MARCH 1992	31. 03. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	BOEHM C.E.

1

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	APPLIED OPTICS vol. 7, no. 5, 1 May 1968, pages 857 - 859; L.COMBES ET AL.: 'FIBER OPTIC POLYCHROMATOR'	1-2
A	US,A,4 812 646 (P.WASZKIEWICZ) 14 March 1989 see column 2 - column 5; figures 2-5	4-6
A	REVIEW OF SCIENTIFIC INSTRUMENTS vol. 59, no. 1, 1 January 1988, pages 125 - 127; J.CASTRACANE ET AL.: 'SIX CHANNEL GRATING SPECTROMETER' see page 125, paragraph I - page 126	1-2
A	US,A,4 711 572 (W.QUILLFELDT ET AL.) 8 December 1987 see column 3 - column 6	1-2

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 9102260 SA 54698

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/03/92. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0362562	11-04-90	DE-A- 3833602	15-02-90
		JP-A- 2147926	06-06-90
		US-A- 4993834	19-02-91
FR-A-2097106	03-03-72	BE-A- 769269	03-11-71
		CH-A- 535949	15-04-73
		DE-A- 2132579	05-01-72
		NL-A- 7109040	04-01-72
US-A-4812646	14-03-89	None	
US-A-4711572	08-12-87	CH-A- 666749	15-08-88
		DE-A- 3436752	13-06-85
		FR-A- 2556093	07-06-85
		GB-A,B 2157420	23-10-85
		JP-A- 60237346	26-11-85

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